

Georgia Institute of Technology
Engineering Experiment Station

and

School of Chemical Engineering
Atlanta, Georgia 30332

FIFTH SEMIANNUAL TECHNICAL REPORT
PROJECT A-661

CHEMICAL REACTIVITY OF HYDROGEN, NITROGEN AND OXYGEN ATOMS
AT TEMPERATURES BELOW 100° K

by

H. A. McGee, Jr. (Principal Investigator), D. B. Bivens, E. Kirschner,
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NASA Grant Nsg-337

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I. INTRODUCTION

There is an important but yet sparsely studied area of chemistry which is concerned with chemical reactivity, chemical synthesis, and molecular energetics of unusual molecules at temperatures usually below 100° K. This area may aptly be called cryochemistry. For chemical rearrangement to occur it is usually necessary that at least one of the reactants be a free radical which may often be produced in copious quantities by pyrolysis or by electric discharge of some suitable parent species. Hence, from an experimental point of view, one has immediate design problems resulting from the necessary proximity of some high energy radical generation operation and a cryogenically cooled reactor.

The results from such studies are interesting from several points of view: (1) synthesis of unusual molecules with interesting properties, (2) synthesis of highly endothermic molecules which are interesting as rocket propellants or perhaps as special purpose additives (this is really a sub-case of (1)), (3) understanding of low temperature chemical phenomena necessary to understanding of comets and the atmospheric chemistry of the Jovian planets, (4) highly increased yields of certain industrial chemicals leading to economically attractive processes, and (5) study of simple species in reaction sequences uncomplicated by "thermal noise" (greatly reduced concurrent and consecutive reactions) which is very attractive in fundamental chemistry. The intent of this NASA grant is most concerned with item (3) and to an extent also with item (2). For example, the most reasonable model of a comet is that of a "dirty snowball" (i.e., frozen ices of C_2H_2 , NH_3 ,

H₂O₂, CH₄, etc. plus meteoric dust) proposed by Whipple.¹

On this basis it seems reasonable that low temperature chemical phenomena are responsible, in part, for the behavior of these objects as observed by astronomers. But none of the above objectives can materialize until all of the common operations of bench scale research in chemistry are adapted to operations at cryogenic temperatures. Hence a significant portion of this research is concerned with these more pragmatic problems of technique. Chemical analysis without prior warmup presents the most difficult challenge in this regard.

II. CURRENT STATUS OF RESEARCH

A. Modifications of Experimental Equipment

1. Sample Injection Capillary

In the apparatus described in previous reports the only type of reaction which could be studied was that between the gaseous atomic species and the second reactant condensed as a liquid or solid. To permit homogeneous gaseous reactions, a sample injection capillary (2 mm OD x 1 mm ID) which was concentric with the atom delivery tube was added to the equipment. The reactant delivery system and the reaction chamber are made of pyrex throughout. The capillary diameter was made as small as possible to minimize the surface area and hence the recombination of the atoms flowing in the annulus parallel to the capillary. The end of the capillary is in the same plane as that of the larger concentric atom inlet tube which permits the gaseous species to mix

¹Donn, B., Formation and Stabilization of Free Radicals, edited by A. M. Bass and H. P. Broida, Academic Press, New York, 1960.

and react as they enter the reaction chamber. One has, in effect, a quenched Polanyi diffusion flame. The second reactant, e.g., nitric oxide or ammonia, enters the capillary through a rotameter and comes in contact with the atomic species at a point 15 mm from the cold surface of the reactor.

2. Inlet System to Mass Spectrometer

Previously, only the crudest analytical studies could be carried out on the reaction products. For example, the temperature and visual appearance of changes in the reaction mass were noted during the warmup period after completion of the initial low temperature reaction. To identify and better study these products, equipment capable of chemical analysis at low temperatures had to be developed. The low temperature capability was essential since most of the products decompose or enter into subsequent reaction while warming toward room temperature. Three possibilities were considered:

1. Use of the previously described liquid nitrogen cooled pipet system to transfer the reaction products from the glass reactor to the cold inlet system of the Bendix T-O-F Mass Spectrometer.

2. Exclusive use of the Bendix T-O-F mass spectrometer and cold inlet system. The atomic species would be produced externally and flow into the cold inlet system where reaction and product identification would occur.

3. Connection of another mass spectrometer and cold inlet system to the existing glass experimental apparatus.

The pipet system is only practical for transferring liquids and since most of the observed reaction products are solids, the pipet system method was rejected. The exclusive use of the Bendix T-O-F machine and cold inlet

system would probably have been the easiest and most practical method to use, however, visual observation of the reaction and the reaction products is not possible with this method. Since it seemed desirable and perhaps necessary to correlate the mass spectra with temperature and reaction product visual changes, the third method was chosen.

A photograph of the system is shown in Figure 1. The inlet system, i.e., the passageway from the reactor to the spectrometer, must be maintained at the same temperature as that of the reactor. This is accomplished by constructing the inlet system from a 1-1/4 in. diameter copper rod which is always partially immersed in the liquid refrigerant in the dewar. The section of copper rod above the refrigerant is vacuum jacketed (10^{-6} mm Hg) and also nickel plated to reduce heat losses by convection and radiation. Calculations have shown that a maximum temperature differential of 1° K might exist from the bottom to the top of the inlet system. As in the cold inlet system used with the Bendix T-O-F machine, this system is connected to a 2 in. long capillary tube which extends into the source structure of the mass spectrometer.

The mass spectrometer which is being used is a small portable magnetic deflection type instrument manufactured by Associated Electrical Industries of England (Model MS-10). The MS-10 has two components, (1) the tube unit and magnet assembly which contains the ion source and collector (visible in the center of the photograph of Figure 1) and (2) the electronic control unit. These two components are connected by 10 feet of cable. This separation facilitated the connection of the small tube unit of the spectrometer to the existing apparatus. The adaptation of this inexpensive instrument for this unusual service has a hidden additional pay-off. The demonstrated utility

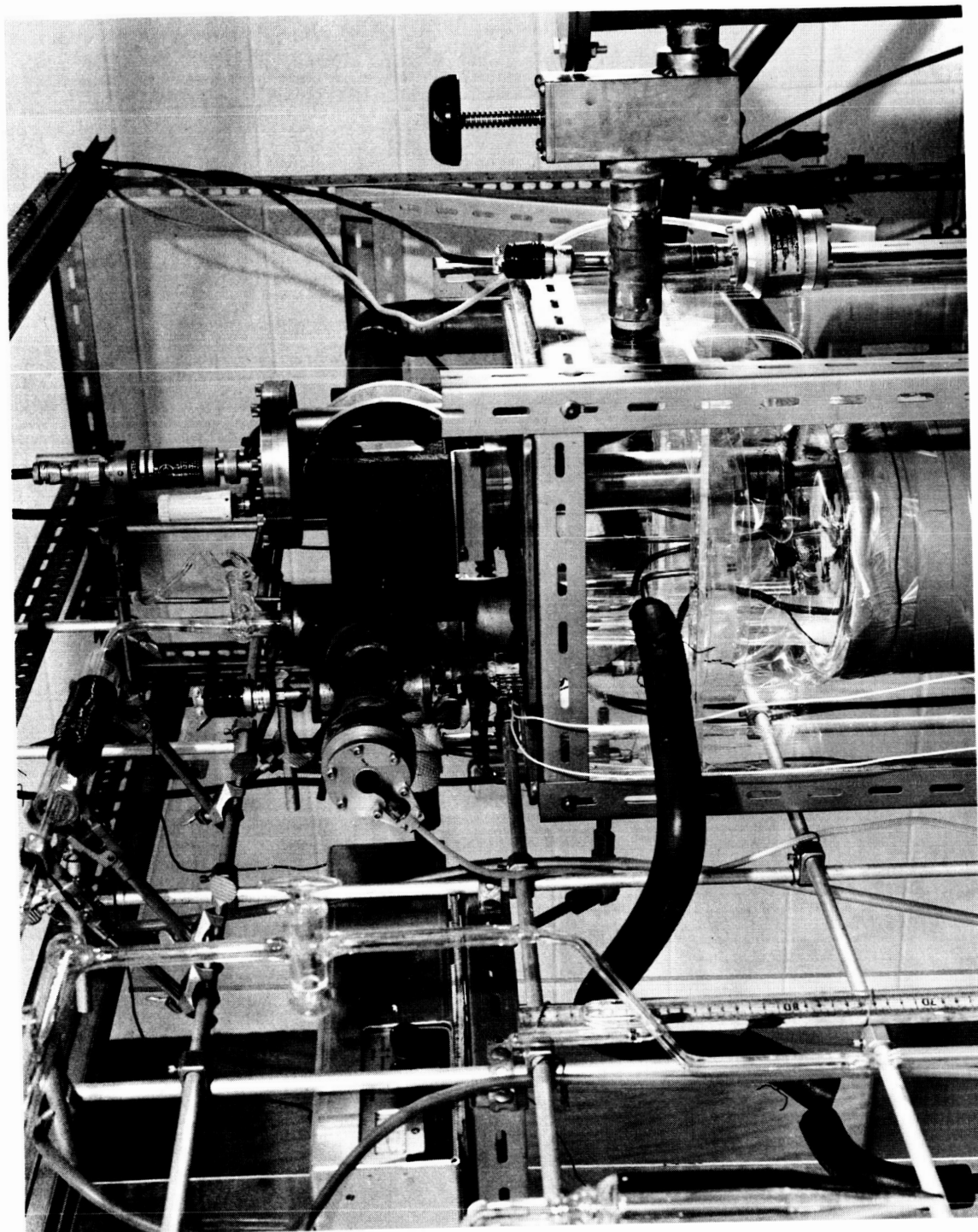


Figure 1. Photograph of Atom Reaction Apparatus

of inexpensive instrumentation will be an impetus for more investigators to enter this new field of chemistry.

A conventional vacuum pumping system of liquid nitrogen cold trap, oil diffusion pump (140 l/sec.) and fore pump is connected to the mass spectrometer tube unit. The connecting lines were made of short length, large diameter pipe to keep the pumping speed in the source as high as possible. After only one collision with any part of the source structure, a sample molecule must be considered background, and hence fast pumping was essential to keep this background below tolerable levels.

The liquid refrigerants presently being used are propane and 2-methyl pentane. Propane has a convenient liquid range of 83° to 231° K (triple point to normal boiling point) and 2-methyl pentane has a similar convenient liquid range of 117° to 333° K. Since both of the liquids are flammable, several safety precautions were necessary. The dewar surrounding the reactor and inlet system and containing the refrigerant was completely enclosed in an air tight plexiglas box. A gas tight flexible connection between the mouth of the dewar and the upper section of this plexiglas structure was made of clear polyethylene film. The top of the plexiglas structure was connected to a 1/4 inch brass support plate through which passed all the controls for operating the experiment. A centrifugal blower exhausting into a hood was connected to the lower part of the plexiglas structure to carry away any gas which inadvertently leaked from the dewared section. In the event of a liquid spill or dewar breakage, the centrifugal blower could also rapidly carry away the flammable gases. To guard against the production of static electricity, all nearby metal parts were well grounded.

Mildly precooled liquid propane or liquid 2-methyl pentane were injected into the dewar, whereupon the liquids were further cooled using a coil through which liquid nitrogen was pumped or by direct mixing of the refrigerant with a stream of liquid nitrogen. To prevent excessive temperature gradients and loss of refrigerant by entrainment in the escaping nitrogen gas, the refrigerant is continually stirred. The stirrer rod enters the structure through a bearing sleeve soldered into the upper brass plate.

The refrigerant temperature is measured using a copper-constantan thermocouple and a millivolt potentiometer. Temperature control presents no problem because of the large volume (about 10 liters) and hence large heat capacity of the well-stirred refrigerant bath. The natural temperature rise is no greater than 10°C per hour. For more rapid temperature increases an immersion heater was used.

Using this equipment, a gas present in the reactor can be moved to the analyzer section of the mass spectrometer without any danger of warming the gas to its decomposition temperature. Therefore, if a reaction product exerts a stable vapor pressure at some temperature, it can be identified.

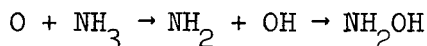
B. Reaction Studies Prior to Installation of Mass Spectrometer

1. Atomic Hydrogen-Nitric Oxide

The reaction of atomic hydrogen and solid nitric oxide at 77°K to produce the explosive yellow product has been described in earlier reports on this grant. Atomic hydrogen has now been reacted with gaseous nitric oxide followed by a rapid quench to 77°K . The explosive yellow product is again formed but in much larger quantities.

2. Atomic Oxygen-Ammonia

The reaction of atomic oxygen and solid ammonia at 90° K to form a light yellow product has previously been described. Atomic oxygen has now been reacted with gaseous ammonia to form a more intensely yellow reaction product. On warming, the unreacted ammonia evaporates first and then the yellow product begins to evaporate. Near room temperature the yellow product either disappears leaving a white product or the yellow product changes to a white product. A small amount of white product, soluble in water, is present in the reactor at room temperature. This compound might be hydroxylamine. Hydroxylamine is a white solid below 33° C, is soluble in water, and could be formed by a reaction sequence,



Hydrazine and peroxide are obvious additional products, and both are to be expected energetically. It was previously postulated that the yellow product might be HNO. However, this is highly improbable since the yellow product formed from the H + NO reaction evaporates at much lower temperatures (about 110° K) than the yellow product formed during the O + NH₃ reaction.

3. Atomic Oxygen-Hydrocarbons

As with the hydrogen atom reactions, the preliminary oxygen atom-hydrocarbon reactions have been carried out in the reaction system without the mass spectrometer. In these investigations, the solid reactants are condensed at 90° K and hence the products from the gaseous reactions are quenched to this same temperature. This temperature was chosen since at lower temperatures dark purple liquid ozone is condensed in the reactor.

Besides interfering with the reactions being studied, liquid ozone is dangerously explosive, especially in the presence of hydrocarbons.

Oxygen atoms have been reacted with acetylene, ethylene, and ethane. Ethylene and acetylene contain the CH and CH₂ groups which have been observed spectroscopically in comets and it was thought that it might also be interesting to investigate the addition of oxygen atoms to the carbon-carbon single, double, and triple bonds.

With acetylene, only the quenched gaseous reaction seems to produce any definite reaction products. This reaction produces a blue flame which can be quenched at 90° K to form a bright yellow solid. On warming, the yellow solid changes to a red, then to a green, and finally to a white solid at room temperature. All during this colorful warmup, a bubbling and frothing of the solid is occurring. On warming the reactor bottom above room temperature with a heat gun, the white solid changes to a yellow polymeric-appearing substance.

With ethylene, the gas-condensed solid reaction and the gaseous reaction followed by a rapid quench apparently produce the same reaction products. At 90° K, the condensed products have a greenish yellow color. On warming, the solids bubble and froth and finally, at room temperature, a small amount of white polymeric appearing material is present.

With ethane, the two types of reactions produce a white reaction product.

The possible reaction products from the oxygen atom-hydrocarbon reactions are probably simple one and two carbon atom compounds containing hydrogen and oxygen atoms. Examples might be ketene, ethylene oxide, formaldehyde, acetic acid, and methanol. The final reaction product from the oxygen atom-acetylene reaction may be glyoxal, C₂H₂O₂. Glyoxal is a yellow crystalline substance

at room temperature, boiling at 50° C, and polymerizing on standing or in the presence of a trace of water.

It is interesting to note the dependence of both the initial reaction product color and the color sequence on warming on the degree of saturation of the hydrocarbon.

<u>Compound</u>	<u>Color Change Sequence on Warming Product</u>
C_2H_2	yellow-red-green-white
C_2H_4	green-white
C_2H_6	white

With the use of the mass spectrometer, this sequence can hopefully be explained.

As mentioned above, the reaction between atomic oxygen and solid acetylene produces no noticeable reaction products. Several possible reasons for this apparent lack of reactivity may be considered. One obvious explanation is that the reaction has an appreciable activation energy. If this is true, at 90° K there probably would not be enough higher energy acetylene molecules to result in reaction. Another possibility is that all of the reactions are only occurring in the gas phase. At 90° K the vapor pressure of acetylene is estimated to be 8×10^{-4} mm Hg and that of ethylene is 3×10^{-1} mm Hg. The apparent reaction between oxygen atoms and solid ethylene might actually be a reaction between oxygen atoms and the vapor phase existing above the solid ethylene.

C. Estimated Thermal Effects in Gas-Solid Reactions

One other factor which should be considered along with the idea of reaction between the atoms and the cold vapor over the condensed reactant is the question

of whether the heat transferred from the gas to the solid plus the heat of any exothermic reactions might cause a significant surface temperature rise. In that case the apparent reaction between the gas and solid might actually be a reaction between the gas and the heated vapors from the condensed solid.

Since measurement of the surface temperature would be difficult and probably inaccurate, calculations of possible surface temperatures for each of the reactions were undertaken. The calculations involved the solving of the following two dimensional heat conduction equations in cylindrical coordinates:

$$\frac{\partial^2 V}{\partial r^2} + \frac{1}{r} \frac{\partial V}{\partial r} + \frac{1}{r^2} \frac{\partial^2 V}{\partial \theta^2} + \frac{\partial^2 V}{\partial Z^2} = 0 .$$

Since the system is symmetrical about the Z axis, the $\frac{\partial^2 V}{\partial \theta^2}$ term is zero. The boundary conditions to be met are

$$V = f(r), Z = 0, 0 \leq r \leq a$$

$$\frac{\partial V}{\partial r} + \frac{h}{K} V = 0, 0 < Z < L, r = a$$

$$\frac{\partial V}{\partial Z} + \frac{h}{K} V = 0, Z = L, 0 \leq r \leq a$$

The following nomenclature was used:

- V = excess emperature, $T - T_0$, where T_0 represents the refrigerant temperature.
- r = radius of cylindrical reactor.
- Z = depth.
- θ = angle around cylinder.
- a = cylinder radius
- L = depth of condensed solid plus reactor base.
- h = coefficient for solid-liquid heat transfer.

K = thermal conductivity.

$f(r)$ = surface temperature distribution.

The heat flow equation with the indicated boundary conditions has been solved to give

$$V = \sum_{n=1}^{\infty} A_n J_0(r\alpha_n) \frac{\alpha_n \cosh\alpha_n(L-Z) + \frac{h}{K} \sinh\alpha_n(L-Z)}{\alpha_n \cosh\alpha_n L + \frac{h}{K} \sinh\alpha_n L}$$

where α_n is defined by

$$\frac{\alpha_n a J_1(\alpha_n a)}{J_0(\alpha_n a)} = \frac{h}{K} a$$

and

$$A_n = \frac{2\alpha_n^2}{a^2 \left(\frac{h^2}{K^2} + \alpha_n^2\right) J_0^2(a\alpha_n)} \int_0^a r f(r) J_0(r\alpha_n) dr .$$

A linear temperature distribution

$$V = f(r) = T_1 - \frac{r}{a} T_1$$

where T_1 is the maximum surface temperature was used in the expression for A_n . This distribution was chosen for the following reason: it had been noticed during experimental runs that concentric color bands which indicated varying film thicknesses were present under and around the area bombarded by the entering gas; this varying film thickness was probably caused by a temperature distribution of the above form. Even if the temperature distribution chosen is not correct, it will still represent an upper limit on the actual distribution. To obtain estimates of the maximum surface temperatures which might occur, the reactions were assumed to be occurring on the surface with

product diffusion into the bulk of the solid. Where estimated physical properties and heat transfer coefficients had to be used, values were chosen which would also produce the maximum surface temperature. The results of the calculations are shown in Table I.

TABLE I
SURFACE TEMPERATURES

Reactant	Surface Temp. Change, °K	Maximum Vapor Pres., mm Hg
NH ₃	90 - 103	< 10 ⁻⁶
C ₂ H ₂	90 - 110	0.018
C ₂ H ₄	90 - 105	1.0
C ₂ H ₆	90 - 106	0.22
C ₂ N ₂	90 - 101	< 10 ⁻⁶
NO	77 - 87	1.4

The low vapor pressures of ammonia and cyanogen suggest that any reaction taking place would definitely be between the hydrogen or oxygen atoms and the condensed solid, i.e., no reaction would be occurring between the atoms and the vapor above the condensed solid. The higher vapor pressures of nitric oxide ethylene, and ethane suggest that some gaseous reaction may be taking place. The vapor pressure of acetylene is intermediate between the two above mentioned cases; however, it has been observed experimentally that no reaction occurs between the oxygen atoms and the condensed acetylene. If this lack of reaction

is only due to the low vapor pressure, then it can be roughly stated that vapor pressures greater than 0.01 to 0.05 mm Hg are necessary for gaseous reaction in the system and equipment being used for these studies.

D. Preliminary Studies Using the Mass Spectrometer and Cold Inlet System

The first reaction that was studied using the mass spectrometer and cold inlet system was that of oxygen atoms with gaseous acetylene. The reaction products were immediately condensed at -136°C using 2-methyl pentane as a refrigerant. 2-methyl pentane has a much lower vapor pressure than propane (1 mm at -61°C versus 1 mm at -129°C) and it seemed reasonable to use the safer refrigerant for the initial work. It was found that the yellow, red, and possibly the green compounds were not formed at this high temperature (-136°C). However, the white frothing solid was formed. During the warmup period, the mass spectra were recorded as a function of temperature. Product species and the temperature of their appearance are given in Table II.

TABLE II

SPECIES IDENTIFIED FROM THE REACTION OF ATOMIC OXYGEN
WITH ACETYLENE WHEN QUENCHED TO -136°C

<u>Compound</u>	<u>Appearance Temperature</u>	<u>Temp. for 1 mm Vapor Pressure</u>
Carbon dioxide	-122°C	-134°C
Formaldehyde	-115°C	-110°C
Ketene	-97°C	-123°C
Acetaldehyde	-97°C	-82°C
Ethylene Oxide	-94°C	-90°C
Methyl Formate	-78°C	-74°C

It can be seen from the table that the compounds appear at a temperature where the vapor pressure is about 1 mm Hg. In this particular experiment, a valve located between the reactor and the main section of the inlet system was only partially opened and this apparently greatly reduced the flow of sample from the reactor to the spectrometer.

In another experiment, the oxygen atom-gaseous acetylene reaction was carried out with the reactor cooled but with the inlet system at room temperature. The reactor was maintained at 90° K using liquid oxygen as the refrigerant and the previously described yellow and red reaction products were formed (also see earlier reports). The dewar of liquid oxygen was replaced with a dewar of liquid propane with a surface temperature apparently near or above -136° C because the yellow and red reaction products immediately disappeared. (No colored products were formed when this reaction was initially quenched to -136° C as discussed above.) The temperature could not be well controlled because a small unstirred dewar was used and large vertical temperature gradients existed in the refrigerant. However, interesting results were obtained from the experiment.

The spectrum of the gases produced during the rapid warmup from -183° C to -113° C included the acetylene peaks and also unexplained peaks at e/m of 45, 32, and 29. The 29 peak is probably the CHO group and the 32 peak probably is excess oxygen formed from the decomposition of the yellow and red compounds. The significance of the 45 peak is presently unknown. The origin of the peaks will be determined in later, better controlled experiments.

In addition to the compounds reported in Table II, the warmup of the reaction products revealed the spectra of formic acid, acetic acid, water, and

possibly glyoxal. The physical appearance of the room temperature product resembled that of glyoxal and a small peak at $e/m = 58$ was observed (parent ion mass of glyoxal). A sample of glyoxal will be obtained to determine a calibration cracking pattern and hence to prove or disprove the above mass assignments.

E. Continued Development of Low Temperature Inlet System for TOF Spectrometer

The development of the cryogenic reactor, purification and inlet system for use with the Bendix TOF mass spectrometer has continued. Some recent results from studies of the synthesis and energetics of the low temperature oxygen fluorides will serve to indicate the utility of the device. These studies, although not themselves of direct interest in the intent of the present grant, do nonetheless represent our present best indication of the functioning of the low temperature system. The oxygen fluoride work has received partial support from our NASA Institutional Grant, Nsg-657.

By way of review, one should realize that the system is designed such that a cold, gaseous sample can be injected directly into the ionizing beam of the mass spectrometer (Bendix TOF, Model 12). For manipulative convenience the cryogenic assembly moves through a vacuum lock arrangement into the spectrometer. In essence, the unit consists of a straight tubular reactor and condensation space with a thermostatted chamber at each end. The temperatures of the two chambers are controlled independently by accurately balancing the heat required to vaporize a finely controlled liquid nitrogen input stream against the heat added by means of a resistance heater which was mounted within each chamber. By varying the liquid nitrogen rate and the heater power,

each chamber could be readily maintained at any temperature above the normal boiling point of nitrogen (77° K). The temperatures were automatically controlled within $\pm 1.0^{\circ}$ K of the desired values by two Leeds and Northrup Speedomax H, AZAR recorder-controllers which operated the heaters in the simple on-off mode.

A mixture of very reactive species can be either injected into or synthesized in the reactor space while both chambers are at some low temperature. Then by raising the temperature of the reactor, a thermal gradient is imposed along a connecting tube between the reactor and the ion source causing the species to be successively vaporized and recondensed at distances along the interconnecting tube which depend upon the volatility of the individual species. Then by manipulating the temperature of each end of the tube, i.e., the two refrigerant chambers, the species may be successively transported through the cold inlet channel and directly into the ionizing electron beam of the spectrometer. A refrigerated nose piece fits directly into the ion source so that the ionizing electron beam is actually in grazing, tangential incidence with the sample inlet hole. Hence, mass spectrometric analysis of the vapors is achieved without warmup above the controlled temperature of the lower refrigerant chamber.

Figure 2 illustrates the general variation of the more interesting ion currents as a function of temperature for the experiments in which O_3F_2 was the principal reaction product. The curves give a composite representation of the ion current intensities observed in three O_3F_2 synthesis runs. In Figure 2, three temperature ranges are apparent (80° - 90° K, 102° - 118° K, and 126° - 150° K) within which significant changes in the mass spectra occur. These

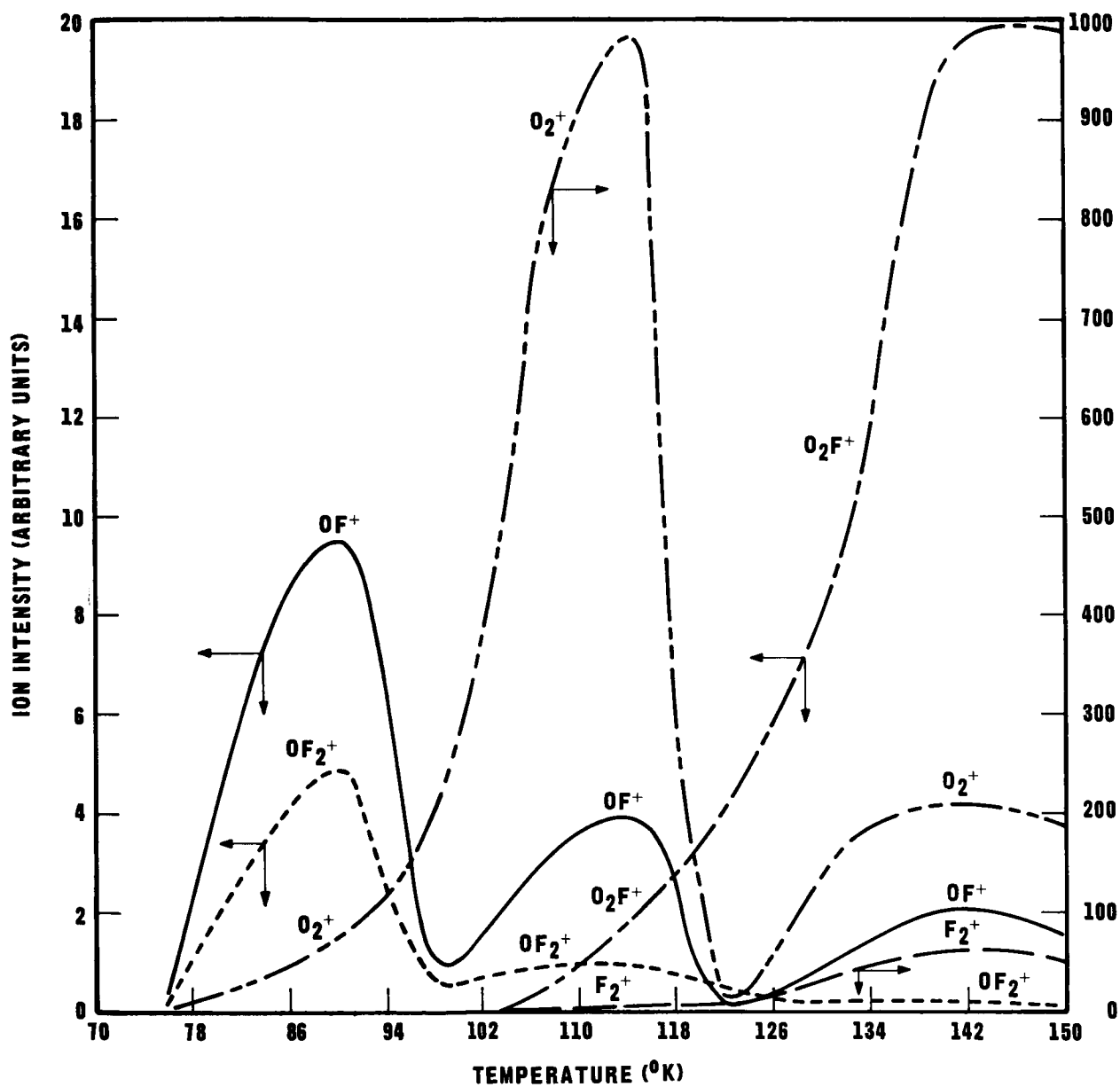


Figure 2. Representative Indication of Variation of Ion Intensities with Temperature from Several O_3F_2 Synthesis Experiments

temperature ranges coincide with the melting point of O_3F_2 (83° - 84° K), the decomposition temperature of O_3F_2 (110° - 116° K), and the temperature region (126° - 150° K) in which O_2F_2 , as a stable entity, exerts a smoothly rising vapor pressure. The vapor pressure of O_2F_2 is 1 torr at approximately 130° K. The parent ion of O_2F_2 ($m/e = 70$) was not observed even when the inlet system was raised above 150° K. A very small signal at $m/e = 70$ was observed only when a very large ion current was present at $m/e = 69$ due to CF_3^+ from CF_4 or C_2F_6 , and was evidently due to the isotope $C^{13}F_3^+$ which is reported to be approximately 1 per cent of the $C^{12}F_3^+$ current.

$A(O_2F^+)$ and $A(OF^+)$ were measured to be 14.0 ± 0.1 ev and 17.5 ± 0.2 ev respectively at 130° K. These values are consistent with other related data and indicate that these ions are being formed by the electron impact fragmentation of O_2F_2 . These numbers permit the partial development of the energetics of the O_2F_2 molecule with results as shown in Table III. Although an effort is now underway, we have not yet measured $I(O_2F)$. Lacking this number, the energetic arguments force one to conclude that the formation of the O_2F^+ ion that was observed here, $O_2F_2 + e \rightarrow O_2F^+ + F + 2e$, was accompanied by about 1 ev of excess kinetic energy. The resulting best estimates of $I(O_2F_2)$ and $I(O_2F)$ are given in parenthesis in Table III.

2. Second Drift Tube Assembly for Bendix TOF Spectrometer

Serious delays in the progress of this research have resulted from the availability of only one mass spectrometer. The actual running time with the instrument, i.e., the time when one is actually performing mass scans or measuring ion currents, is short compared to the time of setting up the high energy radial production apparatus and the cryogenic quenching apparatus

TABLE III

RELATIVE ABUNDANCE AND APPEARANCE POTENTIALS OF POSITIVE IONS IN
THE MASS SPECTRUM OF DIOXYGEN DIFLUORIDE

Ion	Relative Abundance (%)	Appearance Potential (e.v.)	Remarks
$O_2F_2^+$	-	-	$I(O_2F_2) \leq 14.0 \text{ ev}$ ($\sim 13.0 \text{ ev}^b$)
O_2F^+	100	14.0 ± 0.1	$I(O_2F) \leq 13.2 \text{ ev}$ ($\sim 12.2 \text{ ev}^b$)
OF^+	10.1	17.5 ± 0.2	$I(OF) = 13.0 \text{ ev}^c$
O_2^+	(1020) _a	-	$D(FO-OF) = 4.5 \pm 0.2 \text{ ev}$
O^+	(305) _a	-	$D(F-O_2F) = 0.8 \text{ ev}$
			$D(O_2-F) = 0.8 \text{ ev}$
F_2^+	(300) _a	-	$D(OF) = 1.1 \text{ ev}^c$
F^+	(120) _a	-	$D(O-OF) = 4.8 \text{ ev}$

^aIncludes very large background due to decomposition of O_2F_2 in the spectrometer.

^bAccounts for excess kinetic energy in ($O_2F^+ + F$).

^cFrom Dibeler, Reese and Franklin, J. Chem. Phys. **27**, 1296 (1957).

around the mass spectrometer. We now must program the work so that each of several investigators with his own peculiar accessories can be assured of the availability of the spectrometer at certain time intervals.

It is obvious that the rate of experimentation could be effectively doubled by the availability of a second spectrometer. The necessary components

*This work has been described in detail in a paper, J. Phys. Chem. in press, by T. J. Malone and H. A. McGee, Jr. TJM also discussed this work in a paper that he read before the Forty Second Annual Meeting of the Georgia Academy of Sciences, Atlanta, April 23, 1965.

to build a second source-drift tube-multiplier-pumping system complex can be purchased for about \$8600, and this will double the utility of a \$60,000 facility. These components are all on order, but the purchase will not involve expenditures from this NASA grant. This idea of powering two analyzer modules with one control module (all of the electronics) has been thoroughly explored with the instrument manufacturer who assures us that no real problem is involved in the modification. The only connection between the analyzer and control modules are the source and the multiplier plug boxes. Hence, switching the control system from one drift tube to the other should take about one minute.

3. MS-10 Mass Spectrometer

The use of the small spectrometer, Model MS-10 of Associated Electronics Industries, will also tend to alleviate the bottleneck insofar as analysis is concerned (see Section A above). The study of the use of this instrument is important in its own right too, since we can expect more investigators to enter the field of low temperature chemical investigations if adequate analytical instrumentation is available for \$5,000 rather than \$50,000.

4. Infra Red Spectrometer

Mass spectrometry is suitable for analysis only if the unknown substance exerts a usable vapor pressure before it is thermally lost either by decomposition or chemical reaction. In our present arrangements, usable pressure means about 10^{-3} torr. This is not a disadvantage at all if one admits from the outset that he is interested in the synthesis of compounds and in purities and in quantities such that they may be considered to be chemical reagents. In addition, however, it appears that some systems do not exist in the vapor in the same chemical state as they do in the condensed phase. For example, several

laboratories report that O_3F_2 can be distilled at 90° to 110° K with little decomposition. However, when this same distillation is repeated in our cryogenic mass spectrometer inlet system, we obtain no evidence for the species, O_3F_2 , in the vapor phase.

Several groups have very successfully employed low temperature infra-red spectroscopy as an analytical tool in low temperature chemical systems. Clearly the vaporization requirement is here absent. The incorporation of these well developed IR techniques into our existing or planned experimental arrangement is being explored. It appears that mass spectrometry and IR, when applied together, would provide a very high degree of versatility and sensitivity in these cryochemical investigations.

F. Physical Plant

In December of 1964, the entire cryochemistry laboratory was dismantled, moved across the campus to the new \$3,000,000 Chemical Engineering Building and then reassembled. Five laboratory rooms of approximately 20 x 21 ft. are in use, as are five offices. The new facilities provide fully adequate laboratory and office space for a research group of about ten predoctoral and postdoctoral fellows.

G. Personnel

Dr. E. Kirschner has joined our group as a Postdoctoral Fellow in Chemical Engineering. His assignments include a study of the formation and energetics of H_2O_3 and H_2O_4 and an investigation of the advisability of infra-red spectroscopy as an adjunct analytical device to our present reliance upon the mass

spectrometer. IR has, of course, been very successfully used by other groups interested in low temperature chemistry, principally the groups at Berkeley and the Bureau of Standards. Dr. Kirschner is also interested in the adaptation of chromatography as a separative technique for use with our unusual chemical systems at cryogenic temperatures.

Dr. Kirschner has a BS from the Technion in Haifa and is a new PhD from University College, London. Of eleven applicants for the single post doctoral stipend provided by this NASA grant, seven were well qualified and our first choice accepted the appointment.

III. PLANS FOR NEXT REPORTING PERIOD

1. A test compound known to decompose at some low temperature will be synthesized and vaporized into the spectrometer to prove the applicability of the equipment for the identification of low temperature unstable species. If experience shows that the system, as presently designed, operates either poorly or inconveniently, we propose to study the alternative, adaptation of a small quadrupole mass spectrometer for this service. This changeover is particularly simple.

2. The preliminary reactions will be repeated using the mass spectrometer and cold inlet system in an attempt to determine the identity of the unknown reaction products as a function of temperature upon warming of the original reaction product mass.

3. An attempt will be made to determine the relative quantities of compounds formed from the reactions as well as to correlate the qualitative analyses with the energies of reactions insofar as they may be known.

4. The necessary adaptations of the second drift tube assembly to the single electronic control assembly of the TOF instrumentation will be completed. Operations with two drift tubes, and hence a doubled rate of research, should be routine by the end of the next reporting period.